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Journal of Chemical Physics

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Observation of the Cyclic Water Hexamer in Solid Parahydrogen

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We present infrared (IR) absorption spectra of cryogenic parahydrogen solids doped with small water clusters. We observe a sequence of peaks shifted to the red by $\approx 15 \text{ cm}^{-1}$ from the absorptions of cyclic water clusters in liquid helium droplets [K. Nauta and R.E. Miller, Science 287, 293 (2000)]; this sequence includes the peak due to the cyclic isomer of the water hexamer: cyc-(H₂O)₆. We believe this is only the second spectroscopic observation of isolated cyc-(H₂O)₆, and the first report of the IR spectrum of the isolated cluster in the solid phase.

Over the past decade, interest in the spectroscopy of small water clusters, (H₂O)_n, with n = 2 to 10, has grown dramatically.^{1,2} The studies reviewed in refs. 1 and 2 seek to probe systematically the development of water cluster structures, dynamics, and hydrogen-bond (H-bond) interactions with increasing cluster size; one ultimate goal being a better understanding of bulk liquid water and ice. Many recent studies have been performed on gas phase water clusters, for which rotationally resolved spectroscopic techniques can yield very detailed information; e.g.: definitive confirmation of the theoretically predicted lowest-energy cyclic structures of the water trimer, tetramer, and pentamer.

However, it appears that many important water cluster structures may not be amenable to study in the gas phase. The recent observation of the cyclic water hexamer, "cyc-(H₂O)₆," via its infrared (IR) absorption in liquid helium (lHe) droplets³ demonstrates the first production of a non-lowest-free-energy water cluster isomer. By comparison, spectroscopic data from the gas phase water hexamer are once again best explained by the theoretically predicted lowest-energy structure, a compact "cage-(H₂O)₆" isomer.⁴ The preferential formation in lHe of the metastable cyc-(H₂O)₆ isomer is attributed to ring insertion by a water molecule into a cyc-(H₂O)₅ cluster, followed by rapid dissipation of the condensation energy by the lHe, preventing isomerization to a lower energy structure. This expansion of the water cluster "structural landscape"³ beyond that accessible in the gas phase is a notable achievement; however, with the advantage of hindsight, we will show below that it is not unique to the lHe droplet environment.

The stabilization and trapping of metastable chemical species in a non-reactive solid host to permit their leisurely spectroscopic study was an original motivation of the inventors of the matrix isolation spectroscopy (MIS) technique.⁵ Indeed, water clusters have been the subject of numerous MIS studies over the years, however to our knowledge no IR absorption attributable to the matrix isolated cyc-(H₂O)₆ isomer has been reported previously (*vide infra*).

The advantages of solid parahydrogen (pH₂) as a host for

high resolution MIS studies^{6,7} have been recognized and exploited more frequently over the past few years. These advantages derive from the preservation of the spherical nature of the ground state ($v=0, J=0$) pH₂ molecule in the solid phase; the resulting absence of permanent electric multipoles contributes to typically very weak attractive intermolecular interactions. These weak interactions and the small H₂ mass result in solid pH₂ existing as a "translational quantum solid" in which the pH₂ molecules experience large zero-point excursions in a very flat anharmonic potential about their lattice positions.⁸ Solid pH₂ is thus an extraordinarily compressible solid, and an extremely "soft"^{6,7} matrix host, relative to the rare gas solids or other molecular solids typically employed as MIS hosts. The typically weak dopant-pH₂ interactions lead us further to expect minimal perturbations to the dopant's structure and internal dynamics.

Yet, despite this "softness," solid pH₂ is still after all a solid, raising the possibility that the growth of water clusters might be "templated" gently by the lattice, and that the solid might offer some mild steric hindrance against relaxation between (H₂O)_n isomers. Dramatic examples of these effects have been observed by x-ray diffraction of extended water structures confined in much more rigid organic⁹ and organometallic¹⁰ crystalline hosts. Indeed, one-dimensional "tapes" built from H-bond-associated cyclic water hexamers are found to assemble spontaneously within extended channels in an organic host.⁹ Since the nearest neighbor separation in solid pH₂ is $R_{nn} = 3.8 \text{ \AA}$, and the center-of-mass separation in the gas-phase H₂-H₂O complex¹¹ is $R_c = 3.6 \text{ \AA}$, an isolated H₂O molecule should be readily accommodated (perhaps as a nearly free rotor) in a single-substitutional vacancy in solid pH₂. Furthermore, since the separations between oxygen atoms in the cyc-(H₂O)_n family² fall in the range $2.7 \text{ \AA} < R_{O-O} < 3.0 \text{ \AA}$, we expect cyc-(H₂O)_n clusters to fit comfortably in planar n-substitutional vacancies in solid pH₂, where their end-over-end rotations will be quenched but their internal rotational-vibrational-tunneling dynamics may survive intact. An optimist considering the formation of metastable cyc-(H₂O)_n clusters in solid pH₂ would thus hope for effective energetic quenching as in lHe droplets, accompanied by some degree of structural templating, however retaining much weaker perturbations to the final isolated clusters than in the organic and organometallic hosts.

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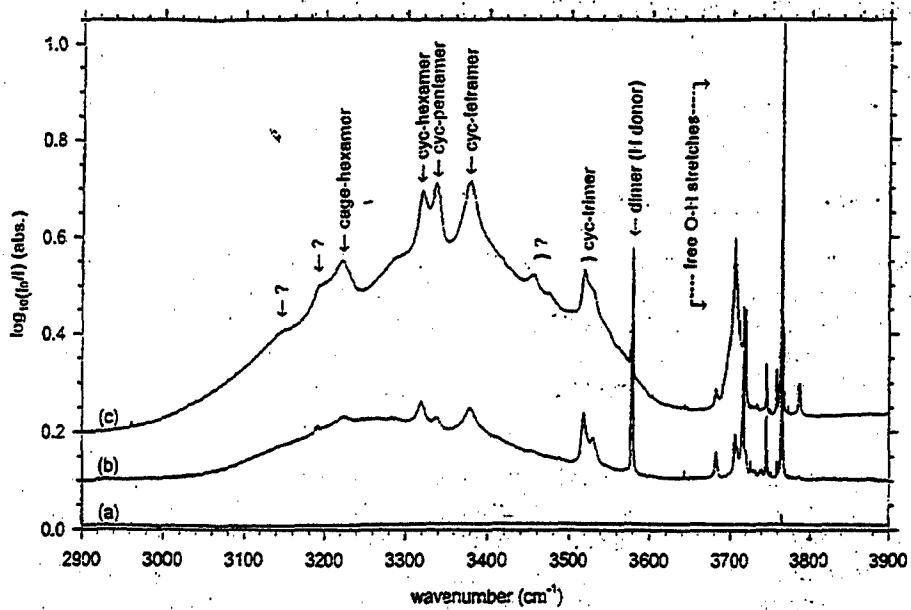


FIG. 1. IR absorption spectra of $(\text{H}_2\text{O})_n$ clusters in solid pH_2 . Trace (a) is for a 3.1-mm-thick, 1000 ppm O_2/pH_2 sample as-deposited at $T = 2.4 \text{ K}$; $\approx 0.5 \text{ ppm H}_2\text{O}$ is also present as an unintentional impurity. Trace (b) is for a ≈ 3 -mm-thick, 140 ppm $\text{H}_2\text{O}/\text{pH}_2$ sample originally deposited at $T = 2.4 \text{ K}$; the spectrum was recorded over a 50 s period during the destructive sublimation of the sample ($T = 10\text{--}3 \text{ K}$). Trace (c) is for the sample depicted in trace (a), after irradiation with ≈ 2400 ArF laser pulses: $\lambda = 193 \text{ nm}$, laser fluence $= 13 \text{ mJ/cm}^2$, pulse duration $= 20 \text{ ns}$, repetition rate $= 5 \text{ Hz}$, $T = 2.4 \text{ K}$. All spectra are presented at 0.5 cm^{-1} resolution, and have been displaced vertically for ease of presentation.

We form $(\text{H}_2\text{O})_n$ clusters in solid pH_2 by two different approaches: (1) thermally induced diffusion and aggregation of initially isolated H_2O monomers, and (2) photolysis of O_2 -doped pH_2 solids. Our photolysis experiments were originally motivated by reports of the exceptional photostability of O atoms in solid nD_2 under 193 nm irradiation,^{12,13} and the attendant implications for chemical energy storage.¹⁴ We will show that a fraction of the O_2 dopant can be driven to reaction with the pH_2 host to produce isolated H_2O molecules and $(\text{H}_2\text{O})_n$ clusters.

Our "Rapid Vapor Deposition" sample preparation technique produces doped, millimeters-thick, optically transparent samples which are ideal for characterization via high-resolution IR spectroscopic methods.¹⁵⁻¹⁹ Briefly: samples are prepared by co-deposition of independent flows of dopant (e.g. H_2O or O_2) and precooled pH_2 gases onto a BaF_2 substrate-in-vacuum cooled to $T = 2 \text{ K}$ in a lHe bath cryostat. We operate our ortho/para H_2 converter¹⁶ at $T = 15 \text{ K}$, yielding $\approx 0.01\%$ residual orthohydrogen (oH_2) content. During a deposition the pressure of uncondensed pH_2 gas remains below $\sim 10^{-4} \text{ Torr}$. Our favorite $\approx 200 \text{ mmol/hour}$ pH_2 gas flow rate results in a solid growth rate of $\approx 3 \text{ mm/hour}$. We use a pulsed ArF excimer laser, $\lambda = 193 \text{ nm}$, for photolysis of the O_2/pH_2 samples. Individual sample preparation details are given in the figure caption.

IR absorption spectra of our samples across the 800 to 7800 cm^{-1} range are obtained using a Fourier Transform IR spectrometer equipped with a glowbar source, a KBr beam-splitter, and a liquid nitrogen cooled HgCdTe detector. To accommodate the IR diagnostic, the entire optical path is enclosed within a 0.5 m^3 polycarbonate box purged with a constant flow of dry N_2 gas.

We begin the discussion of our results by demonstrating the nearly free rotation of isolated H_2O monomers in solid pH_2 , including data from high-resolution IR spectra (not shown) which we will present elsewhere.²⁰ Fig. 1 trace (a) shows the spectrum of a nominally 1000 ppm O_2/pH_2 sample

prior to photolysis; this sample also contains $\approx 0.5 \text{ ppm H}_2\text{O}$ as an unintentional impurity. The small peak near 3765.5 cm^{-1} ($\approx 0.2 \text{ cm}^{-1}$ FWHM) is the $1_{01} \leftarrow 0_{00}$ "R(0)" transition of the v_3 (asymmetric stretch) mode of the para- H_2O monomer; the same feature was previously reported in spectra of UV photolyzed $\text{HI/CO}_2/\text{pH}_2$ samples.²¹ In other spectra of dilute $\text{H}_2\text{O}/\text{pH}_2$ samples (not shown), we also observe the $0_{00} \leftarrow 1_{01}$ "P(1)" and $2_{02} \leftarrow 1_{01}$ "R(1)" transitions of the v_3 mode of the ortho- H_2O monomer at 3719.8 cm^{-1} ($\approx 0.2 \text{ cm}^{-1}$ FWHM) and 3787.1 cm^{-1} ($\approx 2.5 \text{ cm}^{-1}$ FWHM), respectively.

Taking the average of the R(0) and P(1) line positions as the v_3 mode $v=1$ vibrational origin, we estimate: $v_0 = \frac{1}{2} [\text{R}(0) + \text{P}(1)] = 3742.6 \text{ cm}^{-1}$, corresponding to a 13.3 cm^{-1} red shift from the gas phase v_3 origin²² at 3755.9 cm^{-1} , and an $\approx 11 \text{ cm}^{-1}$ red shift from the v_3 origin in lHe ²³ near 3754 cm^{-1} (the v_3 peaks for the H_2O monomer in lHe droplets show linewidths between 3 and 6 cm^{-1} FWHM). The difference between the

TABLE I. Comparison of proton-donor O-H stretching absorptions of $(\text{H}_2\text{O})_n$ in gas phase, in lHe droplets, and in solid pH_2 . All energies reported in cm^{-1} , rounded to the nearest whole number.

| gas phase | lHe droplet | solid pH_2 | $\Delta E(\text{He}-\text{pH}_2)$ | assignment |
|-------------------|---------------------------------------|---------------------|-----------------------------------|--------------------------------|
| 3601 ^a | 3597 ^{c,d} | 3579 | 18 | $(\text{H}_2\text{O})_2$ |
| | 3545 ^c , 3544 ^d | 3531 | 14, 13 | cyc- $(\text{H}_2\text{O})_3$ |
| 3533 ^a | 3532 ^c , 3528 ^d | 3518 | 14, 10 | cyc- $(\text{H}_2\text{O})_4$ |
| | | 3474 | | ? |
| | | 3454 | | ? |
| 3416 ^a | 3394 ^c | 3379 | 15 | cyc- $(\text{H}_2\text{O})_5$ |
| 3360 ^a | 3353 ^{c,d} | 3338 | 15 | cyc- $(\text{H}_2\text{O})_6$ |
| n.o. | 3335 ^{c,d} | 3319 | 16 | cyc- $(\text{H}_2\text{O})_7$ |
| 3220 ^b | 3229 ^c | 3222 | 7 | cage- $(\text{H}_2\text{O})_8$ |
| | | 3192sh | | $2v_2 \text{ H}_2\text{O}$? |
| 3170 ^b | | 3147sh | | $(\text{H}_2\text{O})_{10+}$? |

a - Huisken (1996) b - Paul (1997) c - Frochtenicht (1996)
d - Nauta (2000) sh - shoulder n.o. - not observed

TABLE II. Summary of harmonized assignments of proton-donor O-H stretching absorptions of $(H_2O)_n$ in various matrix hosts. All energies reported in cm^{-1} , rounded to the nearest whole number.

| pH_2 | D_2 | Ne | Ar | Kr | N_2 | assignment |
|--------|---------------------------------------|-------------------|---|---|---|------------------|
| 3579 | 3566 ^c , 3562 ^c | 3590 ⁱ | 3574 ^{a,b} | 3569 ^a | 3550 ^f , 3548 ^e , 3546 ^d | $(H_2O)_2$ |
| | | | 3565 ^f , 3540 ^f | | | ? |
| 3531 | 3525 ^c , 3523 ^c | 3529 ⁱ | 3528 ^f , 3527 ^f , 3525 ^d | | 3510 ^{a,b,f} | cyc- $(H_2O)_2$ |
| 3518 | 3516 ^c | | 3517 ^d , 3516 ^{c,e} | 3514 ^e | | cyc- $(H_2O)_2$ |
| | | | 3500 ^f | | | ? |
| 3474 | | | | | | ? |
| 3454 | | | 3445 ^f | 3435 ^{a,b,f} | | ? |
| | | | 3415 ^f , 3390 ^{a,f} | | | ? |
| 3379 | 3378 ^c , 3375 ^c | | 3374 ^d , 3372 ^d | 3369 ^a | 3355 ^{a,b,f} | cyc- $(H_2O)_4$ |
| 3338 | 3337 ^c | | 3329 ^d , 3327 ^f | | 3320 ^{b,f} , 3318 ^c | cyc- $(H_2O)_3$ |
| | | | 3320 ^f | | | ? |
| 3319 | | | | | | cyc- $(H_2O)_6$ |
| 3222 | | | 3212 ^f , 3209 ^d | 3222 ^a , 3220 ^{b,f} | | cage- $(H_2O)_6$ |
| 3192sh | | | | | | $2v_2 H_2O$? |
| 3147sh | | | 3150 ^f | | | $(H_2O)_{>6}$? |

a - Van Thiel (1957)

b - Tursi (1970)

c - Strommen (1973)

d - Ayers (1976)

e - Murby (1979)

f - Bentwood (1980)

g - Engdahl (1987)

h - Engdahl (1989)

i - Forney (1993)

sh - shoulder

$R(0)$ and $P(1)$ line positions is the sum of the energies of the l_{01} rotational levels in the ground and $v_5, v=1$ vibrational states: $R(0) - P(1) = 45.7 \text{ cm}^{-1}$, which is 96.5 % of the gas-phase $R(0) - P(1) = 47.36 \text{ cm}^{-1}$ separation.²² Thus, both para- H_2O and ortho- H_2O monomers exist as very slightly hindered rotors in solid pH_2 .

The results of two different experiments yielding water clusters isolated in solid pH_2 are also presented in Fig. 1. Trace (c) is the spectrum of the O_2/pH_2 sample depicted in trace (a), following irradiation by the ArF laser. The absorptions in the 2900 to 3600 cm^{-1} region are the "bonded O-H stretches" of proton-donor H-bonded H_2O molecules, those above $\approx 3600 \text{ cm}^{-1}$ are due to free O-H stretches of H_2O monomers and H-bonded H_2O molecules.¹ Restricting our attention further to the bonded O-H stretch region, we note a broad absorption peaking near 3300 cm^{-1} topped by a progression of peaks shifted uniformly by $\approx 15 \text{ cm}^{-1}$ to the red of the absorptions of cyc- $(H_2O)_n$ clusters in IHe droplets.^{3,23} These results, along with the positions of the gas-phase $(H_2O)_n$ cluster absorptions,^{24,25} are summarized in Table I. We note that the broad featureless absorption resembles the spectrum of very large ($n > 10$) water clusters,²⁶ or perhaps that of amorphous ice.²⁷⁻²⁹

While we postpone a detailed discussion of the photochemistry of O_2 in solid pH_2 , we can make a few relevant comments here. We have observed an initial induction period, along with the formation of O_3 and other intermediates, in O_2/pH_2 solids irradiated at 193 nm . We can estimate the final concentration of clustered water molecules in the sample depicted in Fig. 1 trace (c) by integrating the spectrum over the 2900 to 3900 cm^{-1} region; using an effective integrated absorption coefficient for H_2O molecules in ice²⁷ of 1200 km/mol results in a number density of $N_{H_2O} = 6 \times 10^{18} \text{ #}/\text{cm}^3$, or a concentration of $\approx 230 \text{ ppm}$. Alternatively, direct comparison with the $140 \text{ ppm } H_2O/pH_2$ sample depicted in Fig. 1 trace (b) leads to an estimated concentration of $\approx 450 \text{ ppm}$.

Thus only ≈ 10 to 25% of the O_2 molecules in the original $1000 \text{ ppm } O_2/pH_2$ sample had reacted to produce H_2O when the spectrum in trace (c) was recorded, by which point the growth of the $(H_2O)_n$ IR absorptions with further 193 nm irradiation had ceased. This is consistent with the observed chemical reactivity being associated with clusters of O_2 molecules, and not with isolated photo-excited-O atoms.

We assign the peaks in the bonded O-H stretching region by comparison with the IHe droplet results,³ especially the novel cyc- $(H_2O)_6$ cluster peak at 3319 cm^{-1} . The $\approx 15 \text{ cm}^{-1}$ IHe-to- pH_2 red shifts for the cluster peaks are in line with the $\approx 11 \text{ cm}^{-1}$ red shift discussed above for the H_2O monomer. The assignment of the cyc- $(H_2O)_6$ absorption in IHe droplets is based largely on its smooth continuation of the frequency trend observed for smaller cyc- $(H_2O)_n$ clusters, in agreement with the predictions of ab initio calculations.³⁰⁻³² We will use this criterion below to evaluate the MIS literature for a possible previous observation of cyc- $(H_2O)_6$.

To eliminate the possibility that the 3319 cm^{-1} peak is due to an $X-(H_2O)_n$ complex, e.g., $X = O$, O_2 , or O_3 , we produced a $140 \text{ ppm } H_2O/pH_2$ solid and induced-water cluster formation by warming the sample. As in our HCl/pH_2 experiments,¹⁹ warming to $T = 4.8 \text{ K}$ results in extensive clustering, but warming further to $T = 10 \text{ K}$ greatly enhances the 3319 cm^{-1} peak (under these conditions the sample destructively sublimes; however it survives long enough to permit recording a low resolution IR spectrum). The resulting spectrum is shown in Fig. 1 trace (b); again the progression of cyc- $(H_2O)_n$ cluster absorptions is observed, and the relative size of the cyc- $(H_2O)_6$ cluster absorption is enhanced. In contrast, the two unassigned features at 3454 and 3474 cm^{-1} are not reproduced in the pure water doped sample, suggesting that they may be due to an $X-(H_2O)_n$ complex.

We have examined the water cluster MIS literature and found nine reports³³⁻⁴¹ which include data from the 3000 - 3500 cm^{-1} region. We have attempted to "harmonize" these obser-

vations by making tentative re-assignments for peaks originally attributed to water "polymers," the results are collected in Table II. The scatter in the positions of peaks assigned to the same species and host is probably due to a combination of experimental error and the occupation of multiple trapping sites. Examining Table II we see several parallels to the trends from the lHe droplet data for the smaller cyclic clusters, i.e.: the $\approx 145 \text{ cm}^{-1}$ trimer-tetramer shift and the $\approx 40 \text{ cm}^{-1}$ tetramer-pentamer shift. However, there are no examples of the $\approx 20 \text{ cm}^{-1}$ pentamer-hexamer shift, besides the pH₂ results. Thus, while several of the previously reported features remain unassigned, and may be due to other metastable water cluster isomers (!), we conclude that none of them correspond to the cyc-(H₂O)₆ absorptions observed in lHe droplets and in solid pH₂. We do not understand why this is so; we speculate that the elevated temperatures required to induce H₂O recombination in the heavier, more rigid host matrices ($T \gg 10 \text{ K}$) may also promote interconversion between the various (H₂O)₆ isomers.

We have already summarized our major findings above in the Abstract. In the future we will report high resolution IR spectra of H₂O/pH₂ solids including the free-OH and v₂ bend spectral regions.²⁰ We hope that other researchers will recognize and exploit the advantages of solid pH₂ as a host for producing and characterizing H-bonded clusters: the clusters are available in a fixed, stable form and in relatively large absolute quantities and number densities to truly permit their "leisurely study" by experimental techniques not suited to water clusters in the gas-phase or in lHe droplets. We suggest that the path joining the study of small gas phase water clusters with a better understanding of bulk liquid water and water ice may make a profitable detour through an intermediate condensed phase host such as solid pH₂.

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